

MARKED-UP VERSION
OF
AMENDED SPECIFICATION

WO 01/07391

PCT/EP00/06092

Process for the separation and purification of an aqueous mixture comprising the main components acetic acid and formic acid

CROSS REFERENCE TO RELATED APPLICATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a process for the separation and purification of an aqueous reaction mixture comprising the main components acetic acid and formic acid.

2. The Prior Art

The preparation of acetic acid by catalytic oxidation of saturated and/or unsaturated hydrocarbons, for example the gas-phase oxidation of C₄-hydrocarbons, results in formation of product streams comprising as main components acetic acid, formic acid and water in varying proportions.

To work them up further, these product streams have to be separated into their individual components. Separation of a ternary acid/water mixture comprising acetic acid, formic acid and water into its pure components by distillation, for example, presents considerable problems since the system contains not only the binary water/formic acid maximum azeotrope but also a ternary water/formic acid/acetic acid saddle azeotrope.

If such a mixture has a high water concentration, separation by distillation has a tremendous additional energy requirement since all the water has to be distilled off at the top of a column as lowest-boiling component.

- 4 -

about 7% by weight of benzene. The use of benzene in this process and the residual benzene content in the formic acid make this process unattractive.

All the processes known from the prior art are either only suitable for satisfactorily separating binary mixtures such as acetic acid/water, formic acid/water and acetic acid/formic acid or only economically applicable to aqueous acid mixtures in which a high concentration of acid (>60% by weight) is present. Furthermore, some of the known processes are no longer acceptable from the point of view of today's safety and environmental standards because of their use of benzene or chlorinated hydrocarbons.

SUMMARY OF THE INVENTION

It is therefore an object of the invention to provide a process for the separation of a ternary, aqueous mixture of acids into its pure components, which process does not have the disadvantages mentioned in the discussion of the prior art.

It has now been found that the separation and purification of a mixture comprising the main components acetic acid, formic acid, water and high boilers (hereinafter referred to as crude acid) can be carried out particularly readily if the mixture is extracted by means of a solvent in a circulation process in a first step and the extract stream consisting predominantly of solvent, acetic acid, formic acid, high boilers and water is subsequently fractionated in

- 5 -

a sequence of distillation steps into the constituents solvent which is recirculated to the extraction, water, formic acid, acetic acid and high boilers, and the raffinate stream is freed of solvent in a further distillation step by means of a solvent stripping column.

6 The invention provides a process for the separation and purification of an aqueous mixture comprising the main components acetic acid, formic acid and high boilers by extraction with a solvent in a circulation process, which comprises feeding the raffinate stream containing a major part of the water to a solvent stripping column (11) for removal of the water and conveying the extract stream to a solvent distillation column (8) from which, in a first step, a mixture (A) comprising water and solvent is separated off via the top and a mixture (B) comprising acetic acid, formic acid and high boilers is separated off via the bottom, separating the formic acid off from the mixture (B) in column (29) and subsequently fractionating the remaining mixture (B) into pure acetic acid and high boilers in an acetic acid distillation column⁽⁵⁾, and conveying the mixture (A) to a phase separator (25) from which the resulting aqueous phase containing residual solvent is recirculated to the solvent stripping column (11) and the organic phase is recirculated to the extractor (7).

24

BRIEF DESCRIPTION OF THE DRAWINGS

- 6 -

In the first step (extraction) of the process of the invention (Fig. 1), the crude acid feed comprising varying proportions of acetic acid, formic acid, water and high boilers is fed via a line (6) to an extractor (7) and brought into contact with a solvent. The extractor (7) can have a single-stage or preferably multistage configuration. The solvent stream can, in this process, be directed in the direction of flow of the crude acid or preferably be conveyed in countercurrent to the crude acid. Solvents which can be used here are ethers, esters, ketones, alcohols, saturated, unsaturated and cyclic hydrocarbons having from 4 to 8 carbon atoms and their mixtures, preferably ethers and esters having from 4 to 7 carbon atoms, particularly preferably methyl tert-butyl ether, diisopropyl ether, di-n-propyl ether, ethyl butyl ether, ethyl acetate and isopropyl acetate, in a mixing ratio to crude acid (volume/volume) of from 0.5 to 20, preferably from 1 to 5, particularly preferably from 1.5 to 3.5 (ratio volume/volume). The extraction can take place in a temperature and pressure range in which the extraction solvent and the crude acid are present in liquid form and as separate phases, i.e. with a miscibility gap. Preference is given to a temperature range from 0°C to 60°C and a pressure range from $1 \cdot 10^5$ to $20 \cdot 10^5$ Pa.

The raffinate obtained from the extractor (7) is fed via line (15) to the solvent stripping column (11) where pure

- 11 -

additional pure formic acid distillation (33) under lower pressure than in the separation column (29). This results in a significant energy saving together with greatly improved formic acid purity compared with comparable processes. Furthermore, the heat of condensation of the distillation column (29) can be used in an integrated heat system for heating the formic acid distillation column (33) and the solvent column (11). The heat of reaction of the reactions preceding this separation process, for example a catalytic gas-phase oxidation of hydrocarbons, can likewise be used for heating the solvent distillation column (8), the distillation column (29), the formic acid distillation column (33) and the acetic acid distillation column (5).

13
14 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples illustrate the process of the invention with reference to the figures:

Example 1:

In an apparatus corresponding to the embodiment of Fig. 3, a crude acid stream comprising 12.9 kg/h of acetic acid, 2.6 kg/h of formic acid, 48.4 kg/h of water and 0.8 kg/h of high boilers was fed via line (6) to the extractor (7) (countercurrent extraction column with stationary stainless steel packing, organic phase dispersed). Via line (27) and line (14), a solvent return stream containing 135.4 kg/h of methyl tert-butyl ether (MTBE),